

ESR studies of Cu^{2+} doped in triglycine calcium bromide single crystals

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Abstract. Electron spin resonance studies were carried out on Cu^{2+} doped triglycine calcium bromide. The spectra recorded at room temperature revealed well-resolved hyperfine spectra of ^{63}Cu superposed with super-hyperfine lines due to ^{14}N nuclei. The spin Hamiltonian parameters are evaluated. It was concluded that the Cu^{2+} enters the lattice interstitially.

Keywords. Electron spin resonance; Cu^{2+} ; interstitial site; triglycine calcium bromide.

1. Introduction

The properties of cupric ion complexes in biological systems have been the subject of many investigations (Fujimoto *et al* 1973b; Freeman 1966). One of the basic problems is to identify the ion sites and determine the mode of attachment to the host molecules. Studies by Freeman (1966) and Falk *et al* (1967) using ESR spectroscopy are mainly confined to non-crystalline biological materials containing Cu^{2+} ions. But their broad and highly anisotropic spectra allowed no accurate structural analysis.

However, matrices representing the biological environments can be chosen to carry out detailed structural studies. Fujimoto *et al* (1973a) and Fujimoto and Janecka (1971) investigated Cu^{2+} complexes in representative amino acids and obtained detailed information about the magnetic structure. Krishnan *et al* (1978) carried out the detailed ESR studies on Cu^{2+} doped single crystals of diglycine barium chloride monohydrate and suggested that Cu^{2+} enters the lattice interstitially, as well as substitutionally replacing the Ba^{2+} ion simultaneously. The authors have carried out ESR studies on Cu^{2+} doped in triglycine calcium bromide lattice in order to identify the probable sites occupied by the Cu^{2+} ion.

2. Experimental and crystal data

Single crystals of triglycine calcium bromide $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{CaBr}_2$, hereafter referred to as TGCB, were grown from a saturated aqueous solution of stoichiometric proportion of glycine and calcium bromide. The paramagnetic Cu^{2+} ion is introduced during growth by adding 2% cupric chloride to the solution. Natarajan

and Mohana Rao (1976) found TGCB to be orthorhombic with space group $Pbc 2_1$ and unit cell constants $a = 8.97 \text{ \AA}$, $b = 14.74 \text{ \AA}$, $c = 20.80 \text{ \AA}$ and there are 8 molecules per unit cell.

The ESR spectra of TGCB: Cu were recorded at room temperature on an x-band ESR spectrometer assembled in this laboratory, operating at 9.28 GHz employing 100 kHz magnetic field modulation. The spectra were recorded at 10° intervals and DPPH is used as the g -marker. The spectra were recorded in the three principal crystallographic planes *viz.* ab , ac and bc planes.

3. Results and discussions

Figure 1, shows the ESR spectrum of a single crystal of TGCB: Cu at room temperature 20° to the a -axis in the ac plane. This spectrum consists of a single set of four well-resolved hyperfine lines due to the interaction between the unpaired electron of the Cu^{2+} ion and the copper nucleus ^{63}Cu ($S = \frac{1}{2}$; $I = \frac{3}{2}$).

Each lines of the above quartet has a quintet structure with an intensity distribution in the ratio 1 : 2 : 3 : 2 : 1 clearly showing that the quintet is due to the interaction of the unpaired Cu^{2+} electron and the two equivalent ^{14}N ($I = 1$) nuclei. The ESR spectra recorded in ac and bc planes showed a large anisotropy in A and g -values. In the ac plane, the g value varied from a maximum of 2.262 occurring at 10° to c -axis, to a minimum value of 2.071. The corresponding variation in ab plane is very small, where the g value varied from 2.071 to 2.074, indicating an axial symmetry around Cu^{2+} ion in this complex. The g values were determined with an accuracy of ± 0.002 . The experimental angular variation of g^2 and $g^2 A^2$ values has been fitted by the equation

$$g_0^2 = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta,$$

$$\text{and } g^2 A^2 = g_{\parallel}^2 A_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 A_{\perp}^2 \sin^2 \theta.$$

The spin Hamiltonian parameters were evaluated using the Schonland (1959) procedure.



Figure 1. ESR spectra of Cu^{2+} ion in TGCB at 20° to a axis in ac plane.

The angular dependence of the superhyperfine constant A^N for rotation of the crystal in ab and ac planes was investigated. The largest anisotropy was observed in the ac plane. The super-hyperfine constant A^N in this plane varied from 7.3 to 10.8 G.

Table 1 shows the spin Hamiltonian parameters for the Cu^{2+} ion in TGCB:Cu along with those of Cu^{2+} doped triglycine sulphate (Janstankowski and Wieckowski 1974) and dimethyl alanine (Fujimoto and Janecka 1971). The last two copper doped complexes are in N_2O_2 quadrangular site consisting of two nitrogens and two oxygens in trans-position around the cupric ion. The good agreement found in the spin Hamiltonian parameters clearly indicates a similar N_2O_2 environment for Cu^{2+} ion with TGCB:Cu. Further, the quintet structure with the intensity ratio 1 : 2 : 3 : 2 : 1 is itself a clear evidence of the presence of two equivalent nitrogens in trans-position.

The crystal structure indicates that the calcium atom is inside a distorted octahedron surrounded by five oxygens of the carboxyl groups and a bromine atom, with space group $\text{Pbc } 2_1$ and with eight molecules per unit cell. Under this space group symmetry, the Cu^{2+} ions in the unit cell are equivalent in pairs in the principal crystallographic planes and all eight ions are equivalent along the crystallographic axes. Therefore if the Cu^{2+} ion enters the lattice substitutionally at least two sets of Cu^{2+} hyperfine lines should be recorded in any plane except along the crystallographic axes. On the contrary, a single set of Cu^{2+} hyperfine lines was recorded in all the crystallographic planes, clearly indicating that the Cu^{2+} ion does not enter the lattice substitutionally. This is also supported by the low g -values and high hyperfine splitting constant A values and the observation of nitrogen super-hyperfine lines.

Alternatively, as discussed earlier, the Cu^{2+} ion can enter the lattice interstitially with N_2O_2 chromophore. However, due to lack of detailed x-ray crystal structure data, the authors could not locate the interstitial position clearly in this crystal. However, the directions of the g -tensor obtained in these studies, indicate that the plane of $\text{Cu}:\text{N}_2\text{O}_2$ complex is oriented 10° to the ab plane.

Finally when a divalent Cu^{2+} ion enters the lattice interstitially, two positive charges must be set free to bring about charge neutrality. The protons of the ligand amino

Table 1. Spin Hamiltonian parameters for Cu^{2+} complexes at N_2O_2 quadrangular site.

Lattice	Chromophore	g	$A(G)$	$A^N(G)$	Direction cosines		
					a	b	c
TGCB: Cu	N_2O_2	2.071	24	7.3	0.984	0	0.173
		2.074	27	7.3	0	0.974	0
		2.266	162	10.8	0.173	0	-0.984
Triglycine-Sulphate	N_2O_2	2.064	5.2	7.5			
		2.054	30.8	7.5			
		2.261	169.4	11.5			
Dimethyl-alanine	N_2O_2	2.044	20	7.5			
		2.051	18	7.5			
		2.204	152	10.3			

groups could be the ones which are set free in the process of doping, as was suggested by the other studies (Fujimoto *et al* 1973a, b; Chandra Mouli and Sastry 1978). Further studies on optical absorption and ESR spectra at LNT are in progress.

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